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G. M. Carvlin

The Black Forms Of Silver and Mercury.



**THE BLACK FORMS OF SILVER  
AND MERCURY**

**BY**

**GEORGE M. CARVLIN**

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**THESIS**

**FOR THE**

**DEGREE OF BACHELOR OF SCIENCE**

**IN**

**CHEMISTRY**

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**COLLEGE OF LIBERAL ARTS AND SCIENCES**

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

George M. Carvlin

ENTITLED The Black Forms of Silver and Mercury

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Chemistry.

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## A. BLACK SILVER

### I. Introduction.

Silver is capable of existing in a black (amorphous) form possessing qualities differing greatly from those of normal silver. This form of silver, when pure, is a finely divided black powder somewhat resembling platinum black and is broadly distinguished from the normal form by color, by physical properties and by certain chemical reactions.

Black silver has not been investigated very thoroughly hitherto, and the preparation of this substance and the determination of its properties is the purpose of this investigation.

### II. Historical.

Probably the earliest record of experimental work on black silver is found in a paper published by Wöhler in 1839. Wöhler describes in this paper a black compound formed by the reduction of  $\text{AgNO}_3$  by various organic reagents, which he calls silver hemioxide and gives the formula  $\text{Ag}_4\text{O}$ . He was substantiated in this later by Von Bihra.

In 1882, Pillitz published two papers. He commenced by disputing the probability of the existence of  $\text{Ag}_4\text{O}$  on the grounds of valency; namely, as implying that oxygen may be quadrivalent. Pillitz carefully examined the so-called hemioxide precipitated by alkaline solutions of tin and could find no trace of  $\text{Ag}_4\text{O}$  in it.

The first persons to deny logically the existence of Wöhler's series of hemi-compounds of silver appear to have been Newbury and Muthmann working independently some time later. Both, after carefully examining Wöhler's methods, de-



clared the red solution taken by the latter to be argentous citrate, to be a suspension of colloidal silver. At the present time the formation of  $\text{Ag}_4\text{O}$  by Wöhler's method or by any other known method is admitted by no one; so his results must be rejected.

The next and last experimental work performed on this subject and probably the most important bearing on this investigation, was that of M. Carey Lea (1886-91). In a paper published in the American Journal of Science for 1889 he described three distinct allotropic forms of silver. Lea, however, does not furnish positive proof of the existence of these three separate forms and I shall later attempt to point out some defects in his methods.

### III. Experimental.

Lea, in his work upon this subject inferred that silver may exist in three distinct forms: 1st, allotropic silver which may be yellow, blue or green or may have almost any color and may be soluble or insoluble in water; 2nd, the intermediate form which may be yellow, red or green and is almost as indifferent chemically as ordinary silver; 3rd, ordinary silver.

After preparing, according to the method described by Lea, the allotropic form of silver soluble in water, there remained in the solution a colloidal form in the suspensoid state. A precipitation of this form of silver (which we now recognize as "colloidal") takes place both under the action of light and at increased temperatures. This precipitate is black and is not in the least soluble in water.

In order to study the properties of the second modification of silver described by Lea, I precipitated silver nitrate with a solution of ferrous sulphate and sodium citrate, decanted the liquid and then "dissolved" the precipitate in water, the peptization being possibly due to the ferric hydroxide formed from the ferrous sulphate. On the addition of ammonium nitrate the silver separated out.



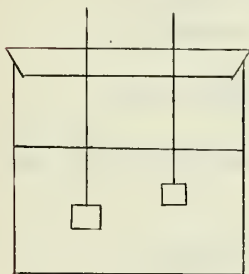


I filtered off this second precipitate, washed it with water containing some ammonium nitrate, and finally with alcohol before drying it over sulfuric acid. The silver so prepared, though not entirely pure, due probably to contamination with a small amount of citric acid, is black and is no longer soluble in water.

The preparation of black silver, which is really coagulated colloidal silver, consists in reducing solutions of silver salts with suitable reducing agents. The methods which I have used are as follows:

#### a. Methods of Preparation.

##### 1. Electrolytic Method.



The cell shown was used to form a silver chloride electrode. By using a normal solution of KCl as electrolyte and a silver anode and platinum cathode, I obtained an even deposit of AgCl on the anode. The average E.M.F. was 8 volts and the average current 0.5 amperes. When the deposit became fairly heavy, I changed the electrolyte to N/1 KOH and reversed the current, making the silver chloride electrode the cathode and the platinum the anode. In this manner, the AgCl was reduced to black silver, forming a smooth black metallic surface on the electrode.

I tried to prepare black silver by this method using freshly precipitated AgCl for the cathode instead of the silver chloride plate. This method was unsuccessful however, due to the low conductivity of AgCl; that is, the solid silver chloride did not function as part of the cathode.

##### 2. Reduction of Silver Nitrate with Ferrous Citrate.

This reaction is slow and gives very low yields. In alkaline solution,





black silver will be formed and in neutral or acid solution, normal silver will come down. The method was discarded as impractical.

### 3. Reduction with Stannous Nitrate.

The silver prepared by this method first forms as a red colloidal suspension. Upon standing for about half an hour, this precipitate coagulates and turns first gray and then black. This coagulation may be hastened by adding a slight amount of sodium or ammonium hydroxide or tartaric acid.

The product prepared by this method is very pure and the yields obtained are satisfactory.

### 4. Reduction with Ferrous Oxalate.

This method of reduction is very slow and not at all satisfactory. The same difficulties are met with in all reductions in organic acid solution.

### 5. Reduction of Silver Chloride with Stannous Chloride.

The silver formed by this method is very impure, as it seems to be adsorbed by  $\text{Sn}(\text{OH})_4$  formed in the solution in the same manner as Purple of Cassius is formed when colloidal gold is adsorbed by stannic hydroxide. If the  $\text{SnCl}_2$  is ground up finely and an excess of  $\text{NH}_4\text{OH}$  is added, the black silver formed, when thoroughly washed with  $\text{NH}_4\text{NO}_3$  and then with  $\text{C}_2\text{H}_5\text{OH}$  shows a purity of about 94.5%. Black silver may never be obtained in a pure state by this method, however, because it is not possible to wash out a considerable amount of the stannic hydroxide. It seems that this phenomenon is one of mutual coagulation of colloids. Colloidal silver is a negative colloid (that is, the suspensoid migrates to the anode) and stannic hydroxide is a positive colloid. It may be assumed that these colloids combine to form some sort of a physico-chemical complex which is quite stable.



6. A solution of tannin (or dextrine) in 10% NaOH was added to  $\text{AgNO}_3$  in excess. The black silver this formed was a fine, amorphous precipitate and the average analysis of six samples was 97.26%. Before analysis these samples were washed repeatedly with  $\text{NH}_4\text{NO}_3$  and finally with  $\text{C}_2\text{H}_5\text{OH}$  after which they were dried at  $60^\circ \text{C}$ .

From the above data it was concluded that the best non-electrolytic methods for preparing black silver are 3 and 6. From the results obtained it seems reasonable to conclude that when silver salts are reduced in alkaline or weak organic acid solution, black silver is formed; while, if the reduction takes place in acid solution, normal gray silver is formed.

According to the thermodynamic point of view, it requires a higher voltage to transfer a gram of silver from the ionic to the metallic form when the silver ion concentration in the solution is low than when it is high. The precipitation of silver from alkaline or organic acid solution, therefore, involves high potential effects, or what corresponds to the same thing, high energy effects or chemical work; consequently silver precipitated from solutions of low silver ion concentration may have a much higher energy content than ordinary silver. That is to say, the silver may form in an allotropic form which is more or less unstable.

#### b. Properties of Black Silver.

##### 1. The Color Reaction.

When amorphous silver is immersed in a solution of a substance readily parting with oxygen, sulfur or halogen, a varied colored film is formed. The coloring of other metals by a film of sulfide or oxide is familiar. With black silver the colors are extremely brilliant.





The substances which produce these reactions are potassium ferricyanide and permanganate, ferric chloride, alkaline hypochlorites and sulfides, solution of iodine, etc. A five or ten percent ferricyanide solution is the best of these reagents because its reaction is more distinctive. Moreover, the action of the latter on normal silver is very slight and here we have a means of detecting the two forms. The composition of the colored film is probably silver ferrocyanide, silver ferricyanide, or a combination of the two.

## 2. Formation of a Continuous Film Upon Drying.

If black silver is taken in a pasty condition and is spread evenly over glass with a fine brush and dried slowly, a perfect black mirror is formed.

## 3. The Halogen Reaction.

When this amorphous form of silver is brushed over paper and the resulting film is exposed to the action of any haloid in solution, very beautiful colorations are obtained. The experiment succeeds best with substances which easily give up halogen, such as sodium hypochlorite, ferric chloride, iodine dissolved in potassium iodide, etc.

## 4. The Action of Acids.

The stronger acids easily convert the black form of silver into the normal gray silver; even acetic acid, not too much diluted, does this.

## 5. Physical Condition.

This black amorphous silver is easily reduced by grinding or pressure to an impalpable powder.

## 6. Amalgamation with Mercury.

Black silver, especially that prepared by the first method above, easily



forms amalgams with mercury, having a smooth, uniform surface exactly like normal silver amalgams.

c. Action of energy on black silver.

1. Action of Electricity.

High tension electricity instantly converts colloidal silver into the normal gray form. A plate of black silver prepared electrolytically was held in the path of a spark of about one inch and gray spots were noticed on the plate after each discharge. The same effect was produced upon a film of black silver on paper. That the gray spots formed in this way are normal silver is easily proved by immersing the piece in a dilute solution of potassium ferricyanide or sodium hypochlorite. The part acted upon by electricity is not affected, while the rest of the film shows the coloration characteristic of colloidal silver.

2. Action of Heat.

When films of black silver on glass or plates formed by the first method above are kept at  $100^{\circ}$  C. for eight or ten hours, there is observed a border of normal silver. At higher temperatures, the change is much more rapid. Here again the ferricyanide test showed complete conversion.

3. Action of Mechanical Force.

The slightest application of force suffices to instantly convert amorphous silver to its normal form. If black silver is spread over a clay plate to dry and is rubbed lightly with a hard surface or even with the finger, the black film is instantly converted to bright metallic silver.





#### 4. Action of Light.

When films of colloidal silver are exposed to direct sunlight, no effects may be noticed for some time. After about a month of this exposure, the sample used had turned to a dull gray color; in two months time this color was slightly more intensified but the sample was not, as we had expected, completely converted to normal silver. It had lost its activity toward ferricyanide solution, however, and from this I am led to believe that a slow conversion was taking place and that, with sufficient exposure the sample would have been completely converted.

This phenomena, I believe, explains the gradual fading of silver photographic prints. If these prints are allowed to stand for several months or years, the image is gradually obscured due to the conversion of the silver from its black amorphous form to the ordinary form. This difficulty is overcome in practice by toning the prints with gold or platinum, thus replacing the silver by these more permanent elements.

#### d. Analysis.

The purest samples of black silver which I was able to obtain contained about 97% silver, the rest being occluded tin in the third method, and organic acids in the other methods. Black silver prepared by the electrolytic method seems to be the purest obtainable, however, and upon this was based the most conclusive evidence of the existence of pure silver in the black form.

I determined the electrode potential of a uniform plate of black silver and found it to be 0.6976 volts, while that of normal metallic silver was found to be 0.6988 volts. The divergence of 0.0012 volts is within the experimental error, so that black silver is, without a doubt, pure silver.

This result was rather surprising, as I expected that the more reactive



amorphous form of silver would have a decidedly lower electrode potential than the normal form.



## B. BLACK MERCURY

### I. Historical.

The fact that mercurous salts give black derivatives with ammonia is one of the earliest records of chemistry. It is surprising, therefore, that so little attention has been given to the ultimate nature of the black substance. There are in general two theories to account for this phenomenon: First, the formation of a black dimercuro-derivative, as  $\begin{matrix} \text{Hg} - \text{NH}_2 \\ \text{Hg} - \text{Cl} \end{matrix}$ ; second, the breaking down of the mercurous nucleus  $\begin{matrix} \text{Hg} - \\ \text{Hg} - \end{matrix}$  into  $\text{Hg} =$  and free mercury, the latter being black. This view is borne out by such phenomena as the following. If a smear of the black precipitate formed by the action of ammonium hydroxide on calomel is placed on a glass slide, the color gradually changes over to a gray, with a steady loss in weight. This is attributed to the loss of the black mercury by volatilization.

### II. Experimental.

#### a. Methods of Preparation.

##### 1. Stannous nitrate reduction.

##### 2. Formation of a complex.

In the latter method, the mercury complex comes down as a fine white precipitate and partially obscures the black mercury formed.

3. Black mercury may also be prepared by adding a solution of dextrine or tannin in NaOH to a solution of  $\text{Hg}_2(\text{NO}_3)_2$ .

The first and third methods seem to give the largest yields and the purest





product. The average analysis of six samples formed by the last method gave 96.87% mercury.

I am inclined to believe that the black product obtained by exposing mercurous chloride to sunlight is black colloidal mercury, though it may be, as Lea suggests, a mercury subchloride.

#### b. Properties of black mercury.

The properties and reactions of black mercury are the same as those given for black silver. One interesting property of colloidal mercury is that of amalgamating with gold and silver. It forms these amalgams as readily as does normal mercury, and they are uniform and smooth and exactly the same in every way as normal amalgams.

#### IV. Conclusion.

From the results obtained in this investigation, I have concluded that the vari-colored substances obtained by Lea were not, as he inferred, allotropic forms of silver but rather colloidal silver in different stages of coagulation. The fact that both forms of silver have identical electrode potentials indicates that the black silver may not be in the allotropic condition, but rather is in a completely coagulated colloidal state.

Whether silver shall be reduced from its compounds in the metallic or amorphous form depends upon the reducing agent applied; so that it cannot be said with any certainty in which condition it is present in its compounds.

Lea, in concluding his work on this subject, suggests that in the black form, silver is in the atomic condition and that, in the conversion from the black to the normal form which is in the molecular condition, a polymerization takes place.





It seems more probable, however, in view of the greater reactivity of the black form, that the latter is merely a different condition of the same silver and that in the conversion to normal silver, no essential change in the structure of the molecule takes place.

Much useful work may be accomplished in finding practical applications for these two colloidal substances, probably as a catalyst to replace the more expensive forms of platinum and palladium. I tried black silver and mercury as a catalyst in connection with various organic reductions in which platinum black has been used heretofore, but did not achieve any noticeable success. Both will decompose hydrogen peroxide, but much more slowly than platinum black.

These two elements are not, in all probability, the only ones possessing these peculiar amorphous forms. Copper, bismuth and some other metals give promise of existing in more than one form.



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